"Laboratory Studies of Low Temperature Rate Coefficients: The Atmospheric Chemistry of the Outer Planets"

Progress Report for January 1994 to November 1994

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1 January 1994 - 1 November 1994

The objectives of the research performed under NASA grant NAGW-2438 are to measure laboratory rate coefficients for key reactions relevant to the atmospheres of Titan and Saturn. These reactions are, for example, $C_2H + H_2$, CH_4, C_2H_2, and O_2, which need to be measured at low temperatures, down to ≈150 K. The results of this work will be provided to NASA specialists who study modeling of the hydrocarbon chemistry of the outer planets. The results are also expected to reveal important principles about the low temperature chemistry, such as the formation of adducts for intermediates and possible enhancement of the rates due to quantum mechanical tunneling.

The experimental apparatus is fully operational, and work has been published on two systems, $C_2H + C_2H_2$ (Pedersen, Opansky, and Leone, 1993) and $C_2H + O_2$ (Opansky, Pedersen, and Leone, 1993). Detailed reports on these reactions have also been provided previously. Three aspects of the work have been our focus thus far in 1994. (1) Measurements were performed to obtain the rate coefficients as a function of temperature for $C_2H + CH_4$ and CD_4. (2) Improvements to the laser pulse/probe system were implemented to enhance the signal-to-noise. (3) An experimental set-up was constructed to attempt laser-induced fluorescence detection of C_2H. A brief description of these results will be provided.

The photolysis of acetylene by solar flux, which results in C_2H, can react with methane to catalyze the dissociation of methane to form CH_3 (methyl radicals). The recombination of two methyl radicals produces ethane, which can then be transported downward and accumulate on the surface:

$$C_2H_2 + h\nu \rightarrow C_2H + H$$
$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$$

$$\textit{then}\ \ CH_4 \rightarrow CH_3 + H$$
$$\textit{net}\ \ CH_3 + CH_3 \rightarrow C_2H_6$$

Thus the reaction of C_2H with CH_4 is critically important in the planetary atmospheres. The rate coefficients for the reaction of $C_2H + CH_4$ at room temperature were previously reported by Laufer (1981) as 1.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, Renlund *et al.* (1981) as 4.8×10^{-12}, Lander *et al.* (1990) as $3 \pm 0.3 \times 10^{-12}$. The measurements in our laboratory obtain $2.7 \pm 0.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 300 K for CH_4 and $1.1 \pm 0.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for CD_4 (Opansky, Pedersen, Leone 1994).

Brown and Laufer (1981) used bond energy-bond order calculations to obtain the Arrhenius A factor, and they described the temperature dependence as 3×10^{-12} (exp(-250/T)). We find a steeper temperature dependence for the $C_2H + CH_4$ reaction, characterized by the form 1.42×10^{-11} exp(-(547±36)/T) cm^3 $molecule^{-1}$ s^{-1}. For CD_4, the activation energy is 9% higher. However, the relatively small activation energy suggests that the $C_2H + CH_4$ rate coefficient does not decrease as rapidly as the value for the $C_2H + H_2$ reaction at low temperatures. For example, unless there is a change in the mechanism with temperature, C_2H + methane will have a rate coefficient of 6×10^{-14} at 100 K while the expected rate coefficient with H_2 will be only 3×10^{-16}. Small differences in the forms of the rate coefficients are magnified at low temperatures, and thus our revision to the Arrhenius expression takes on important significance. A direct comparison between the low temperature reactivity of C_2H with CH_4 versus H_2 is of critical importance to the interpretations of the hydrocarbon ratios in the planetary atmospheres. In work soon to be pursued in our laboratory, direct comparisons of the reactivity of C_2H with CH_4 and H_2 will be made with a single apparatus. The work will be extended to C_2H reactions with other hydrocarbons, such as ethane (C_2H_6) propane (C_3H_8), as noted below.

To measure very slow rates, the signal-to-noise at very low pressures of the acetylene photolysis precursor is essential. We discovered in measuring the CH_4 and CD_4 systems that often we were not able to investigate a wide enough range of pressures because the signal-to-noise became too low. Therefore, we initiated a series of improvements to the tunable F-center probe apparatus to acquire more signal. We built a multipass arrangement for the tunable F-center laser, so that we could obtain a factor of 2-3 improvement in the absorption pathlength. This was successful, and it resulted in the construction of a new cell and a sophisticated optical arrangement to multipass and align the laser. Since the multipass arrangement diminishes the power of the F-center laser falling on the detector, we also explored using other detectors which have higher intrinsic responsivity. We attempted to employ a liquid helium cooled detector, which was available in our laboratory and in principle would give more signal amplitude. However, we found that one of the wires had been fractured at the detector element, and after several attempts to repair it and many cool-downs, we concluded that the unit was unfortunately beyond repair. Our efforts then turned to improving the single mode power from the F-center, which was achieved.

While these improvements were being made, our krypton ion pump laser had a catastrophic failure of the electrical cable system. Coherent Radiation did not want to attempt to repair this laser, instead opting to send us a new laser to use under our warrantee. Eventually we will have to pay for this laser, which we hope to be able to do with other funds. During the time that the krypton ion laser was down and we were waiting for the new one to arrive, we decided to try to develop a set-up to attempt laser-induced fluorescence (LIF) detection on the C_2H radical. There is one group that has reported a successful detection of C_2H by LIF using an unassigned upper state (Hsu, *et al.* 1992, Hsu *et al.* 1993). The detection can be accomplished on a transition from the vibrationally excited bending state, (0,1,0), which is sufficiently low in energy that it will be thermally populated in the flow cell. We set up a different configuration of the flow

cell which included baffle arms for perpendicular two-laser experiments. In this cell we can produce C_2H by photolysis of acetylene at 193 nm and excite the C_2H with a frequency doubled dye laser. A few brief attempts to observe the LIF have been made, but no signal has yet been detected, most likely because of problems due to scattered laser light. However, the work is still in progress and if successful will permit a possible new way to acquire kinetics results with greater sensitivity. Recently a new krypton ion laser has been shipped to us, and our immediate goals are to return to the F-center laser probe measurements which were working well until the old krypton ion laser failed.

Planned Work

1 January 1995 - 31 December 1995

Immediate work to be pursued will be a study of the reaction rate coefficients of $C_2H + H_2$, ethane, propane, and butane at lower temperatures. The lower vapor pressures of the larger hydrocarbons may limit the lower values of the temperature that can be achieved with the present cell. We have ordered a sample of CF_3C_2H, which will be used as the precursor of C_2H for the important studies of $C_2H + H_2$. The much slower reaction of C_2H with CF_3C_2H, compared to the reaction of C_2H with C_2H_2, will be helpful to measure the very slow reaction of C_2H with H_2. In addition, the laser multipass signal enhancement will be an important improvement for these studies. These investigations will provide important data on quantum mechanical tunneling probabilities, which are essential for isotopic fractionation. Finally, there is very little work on the reactions of C_2H with nitrogen containing compounds, such as HCN, CH_3CN, etc. Since the coupling of the carbon chemistry and nitrogen chemistry is an important process in the atmospheres of the outer planets, we intend to direct our studies along these lines in the near future.

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